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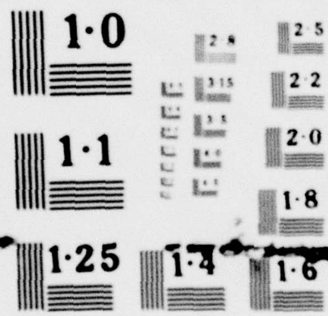
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FJSRL TECHNICAL REPORT - 79-0011

NOVEMBER 1979

OPTIMIZATION OF $LiAl/NaAlCl_4/CuCl_2$ THERMAL CELLS

CAPT ROBERT L. VAUGHN

PROJECT 2303

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AIR FORCE SYSTEMS COMMAND

UNITED STATES AIR FORCE

FJSRL-TR-79-0011

This document was prepared by the Electrochemistry Division, Directorate of Chemical Sciences, Frank J. Seiler Research Laboratory, United States Air Force Academy, Colorado. The research was conducted under Project Work Unit Number 2303-F2-07, "Pelletized Thermal Batteries". Captain Robert L. Vaughn was the Project Scientist in charge of the work.

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The optimization of $LiAl/NaAlCl_4/CuCl_2$ single thermal cells is presented. Energy densities were obtained over the temperature range 175-275°C and current density range 15-150 mA/cm^2. The results were compared to similar data for $LiAl/NaAlCl_4/MoCl_5$ and $LiAl/NaAlCl_4/FeCl_3$ cells. Although the $CuCl_2$ type cell had a lower voltage than the other types, its energy density was higher due to the extended lifetimes of these cells.

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OPTIMIZATION OF $LiAl/NaAlCl_4/CuCl_2$ THERMAL CELLS

By

Capt Robert L. Vaughn

TECHNICAL REPORT FJSRL-TR-79-0011

November 1979

Directorate of Chemical Sciences
Frank J. Seiler Research Laboratory
Air Force Systems Command
US Air Force Academy, Colorado 80840

PREFACE

This report documents work done under Work Unit 2303-F2-07, Pelletized Thermal Batteries, between 2 February and 21 September 1979.

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INTRODUCTION

Copper(II) chloride, molybdenum(V) chloride, and iron(III) chloride have been investigated in our laboratory as cathode materials in thermally activated cells using sodium tetrachloroaluminate electrolyte (1,2,3). The study of $MoCl_5$ and $FeCl_3$ cells included the optimization of the cell configuration with some consideration of cathode material particle size. However, the $CuCl_2$ study considered only $CuCl_2$ particle size, quantity and purity of graphite used in the cathode, and LiAl alloy composition. The study did not attempt to arrive at a best component configuration.

Due to technical problems associated with the $LiAl/NaAlCl_4/MoCl_5$ battery development (4), $CuCl_2$ has increased in importance as a possible cathode material in a chloroaluminate battery. Therefore additional study was required to arrive at an optimum configuration for $LiAl/NaAlCl_4/CuCl_2$ thermal cells. This report presents the optimization of $CuCl_2$ single cells and compares their discharge behavior to $MoCl_5$ and $FeCl_3$ cells.

EXPERIMENTAL

The electrolyte preparation, cell fabrication, and test procedures were the same as used previously (2,3).

The starting point for $CuCl_2$ cell optimization was based upon the optimum configurations that had been obtained for $FeCl_3$ and $MoCl_5$ cells. The configurations of these two cell types were similar in that they had the same anode composition and the same cathode composition except for the amount of active cathode material. The only other configuration difference was the amount of separating electrolyte.

Two $CuCl_2$ cells were made and tested under the same operating conditions. The first cell was made using the $MoCl_5$ cell composition and produced 30.1 Wh/kg

to 80% of the initial closed circuit voltage (ICCV). The second cell had the same composition except that the $FeCl_3$ cell separator weight was used. This cell produced 33.0 Wh/kg, therefore the $FeCl_3$ separator weight was taken as the optimum for the purpose of this study.

The weight of $CuCl_2$ in the cathode was determined by a series of cell tests in which the weight of $CuCl_2$ was varied. The results, shown in Fig. 1, indicated that 1.5g was the best weight. Table I shows the final composition of $CuCl_2$ cells used in this study.

TABLE I. Configuration of $CuCl_2$ Single Cells

Anode	0.27g LiAl (60.2 a/o) 0.12g EBM*
Separator	0.99g EBM*
Cathode	0.64g EBM* 1.50g $CuCl_2$ 0.23g C

*90 w/o electrolyte (49.85 m/o $AlCl_3$, 50.15 mo NaCl) and 10 w/o SiO_2 binder

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The $CuCl_2$ used in this study was anhydrous, 51.3% Cl supplied by Alfa-Ventron Corp. and was used in this study as received without regard to particle size. The graphite was Fisher grade 38 and was used as received.

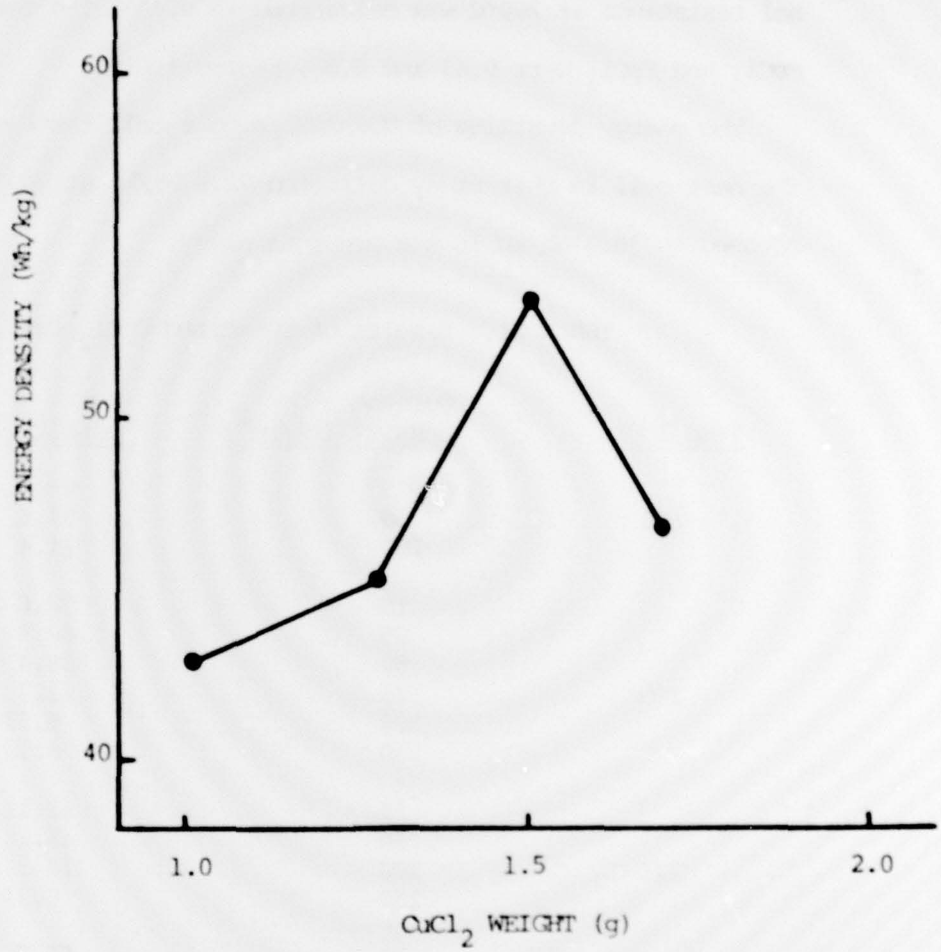

FIGURE 1. Optimization of $CuCl_2$ Weight

RESULTS AND DISCUSSION

The open circuit voltage (OCV) for the $CuCl_2$ cells was 1.85v at 200°C, whereas the values for $MoCl_5$ and $FeCl_3$ were 2.4 and 2.3v, respectively. The ICCV as a function of current is shown in Fig. 2. From this plot, the internal resistance at 200°C was calculated as 0.43Ω. The corresponding values for $MoCl_5$ and $FeCl_3$ were 0.63 and 0.5Ω, respectively.

The energy densities of the $CuCl_2$ single cell tests are given in Table II. The best cell in this study delivered 72.6 Wh/kg at 200°C and 15 mA/cm^2 as opposed to 30.3 Wh/kg in the previous study.

TABLE II. Results of Optimized $CuCl_2$ Cell Tests

Temp (°C)	Current Density (mA/cm^2)	80% Density (Wh/kg)
	15	67.4
175	50	33.6
	100	11.4
	15	72.6
	25	60.9
	50	38.4
200	75	21.7
	100	9.78
	150	8.13
	15	62.1
	50	46.1
225	100	18.1
	150	8.34
	15	61.2
250	50	53.8
	100	20.8

Despite their lower voltage, $CuCl_2$ cells delivered greater energy densities than the other types of cells due to long lifetimes. The best $CuCl_2$

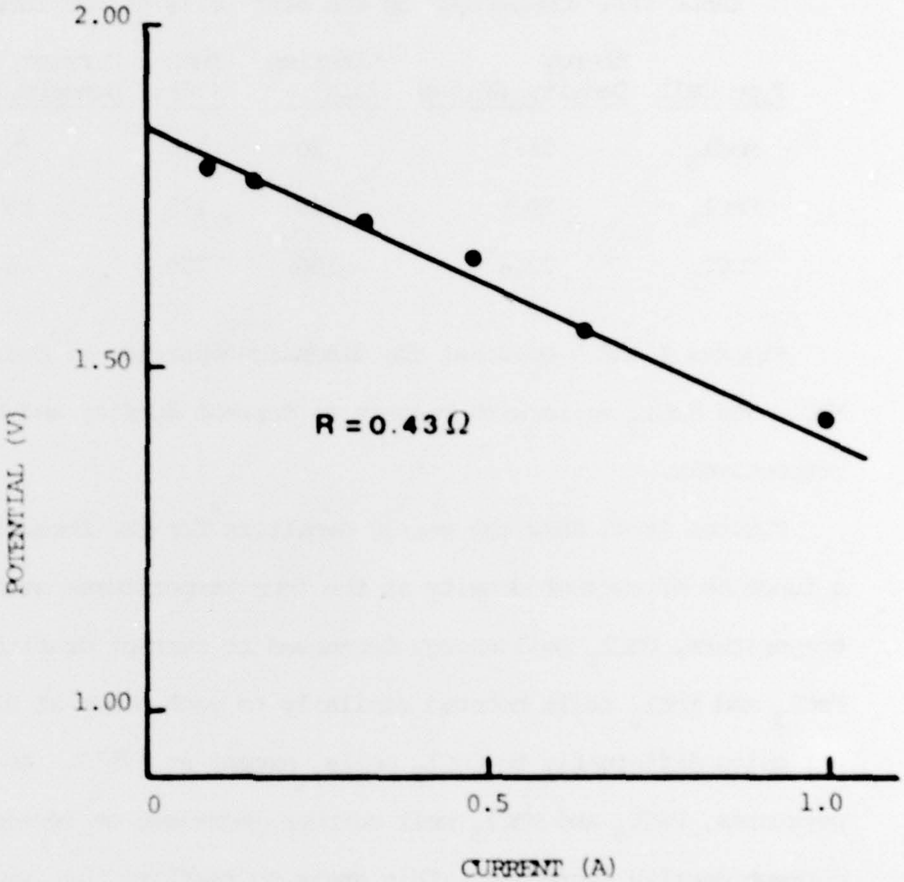

FIGURE 2. Internal Resistance for $LiAl/NaAlCl_4/CuCl_2,C$ Cells at 200°C

cell had a lifetime to 80% ICCV of 106 minutes, almost twice that of the best $FeCl_3$ cell. Discharge curves for the best cell of each type are shown in Fig. 3 and Table III compares the best energy densities obtained from the three types of cells.

TABLE III. Comparison of the Best Cells of the Three Types

Type Cell	Energy Density (Wh/kg)	Lifetime (min)	Temp (°C)	Current Density (mA/cm^2)
$MoCl_5$	36.7	30	175	15
$FeCl_3$	50.6	58	175	15
$CuCl_2$	72.6	106	200	15

Figures 4 and 5 contrast the discharge behavior of $CuCl_2$ cells with $MoCl_5$ and $FeCl_3$ cells with respect to current density and temperature, respectively.

Figures 4a-4d show the energy densities for the three types of cells as a function of current density at the four temperatures studied. At every temperature, $CuCl_2$ cell energy decreased as current density increased. $FeCl_3$ and $MoCl_5$ cells behaved similarly to each other at all temperatures but quite differently to $CuCl_2$ cells, except at 175°C. At the higher temperatures, $FeCl_3$ and $MoCl_5$ cell outputs increased or leveled off as the current density increased. This seems to reaffirm the assertion made in the earlier study that $CuCl_2$ are low current type cells as opposed to $MoCl_5$ and $FeCl_3$ cells.

However, the $CuCl_2$ cells in this study performed better than the other types of cells at current densities as high as 60 mA/cm^2 at 175°C and 200°C (Fig. 4a and 4b) and as high as 80 mA/cm^2 at 225°C (Fig. 4d). While $CuCl_2$

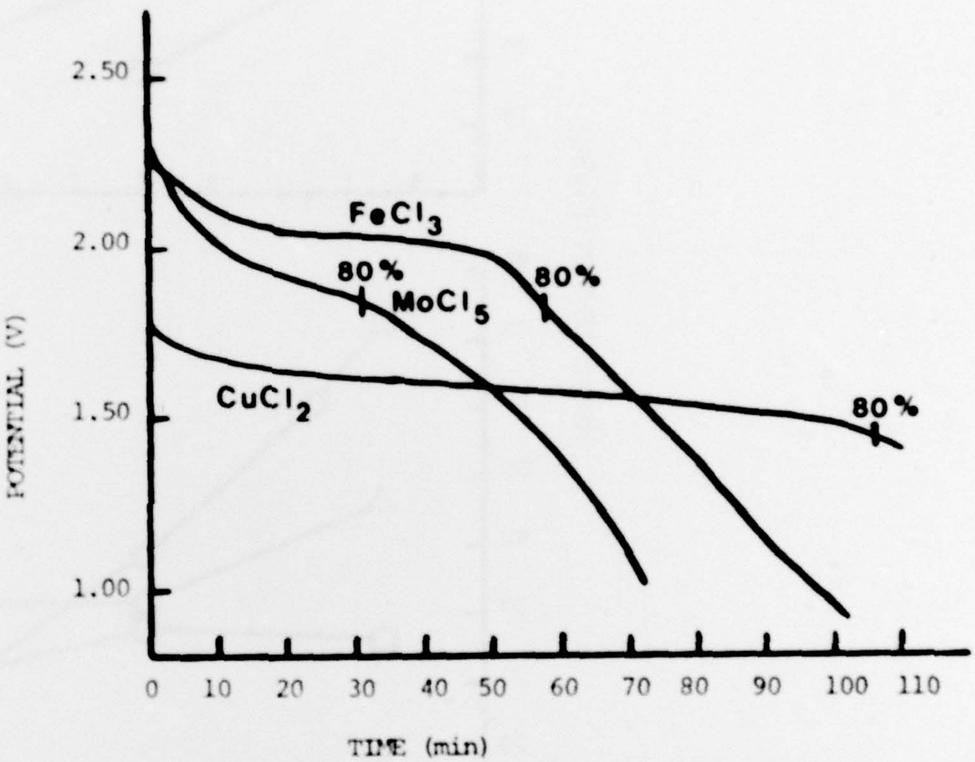

FIGURE 3. Discharge Curves for the Best Cell of Each Type

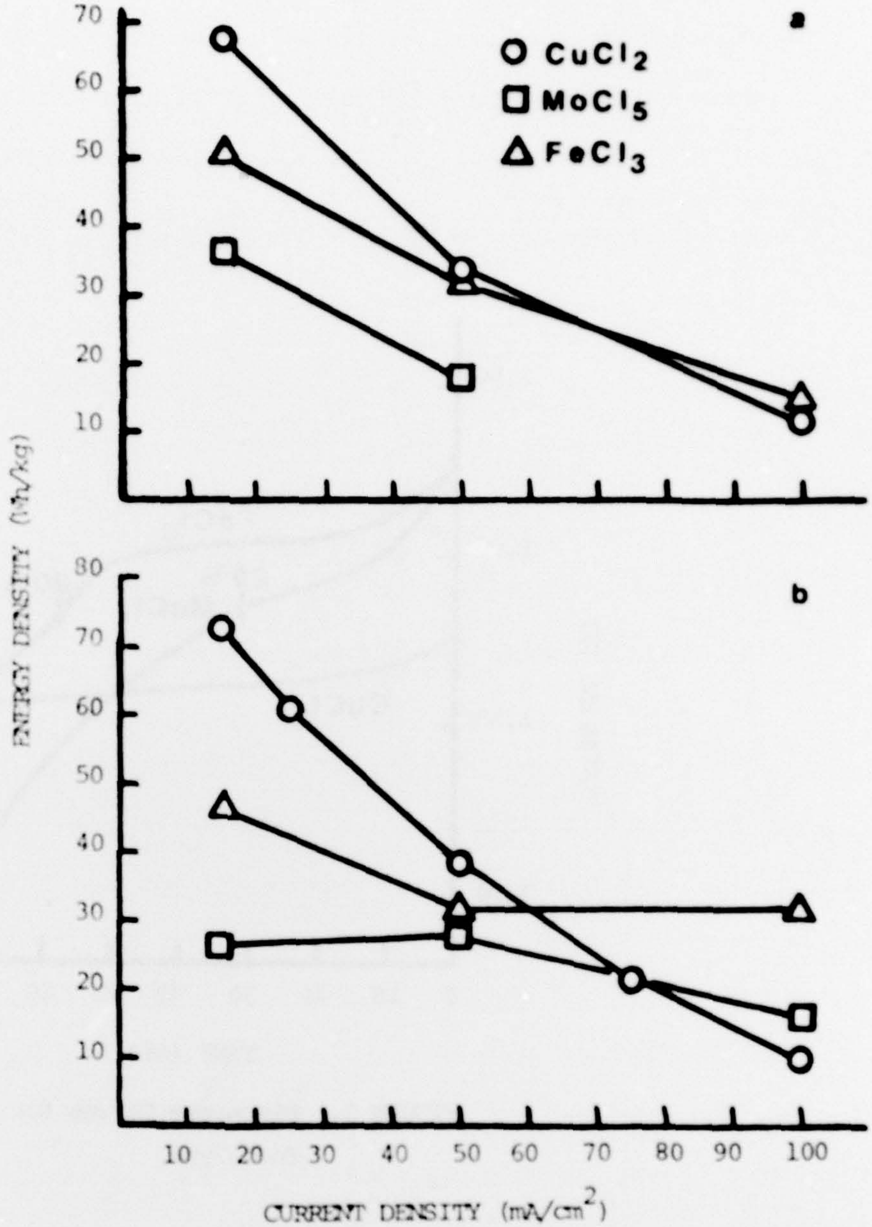

FIGURE 4. Energy Density as a Function of Current Density at a. 175°C, b. 200°C, c. 225°C, and d. 250°C.

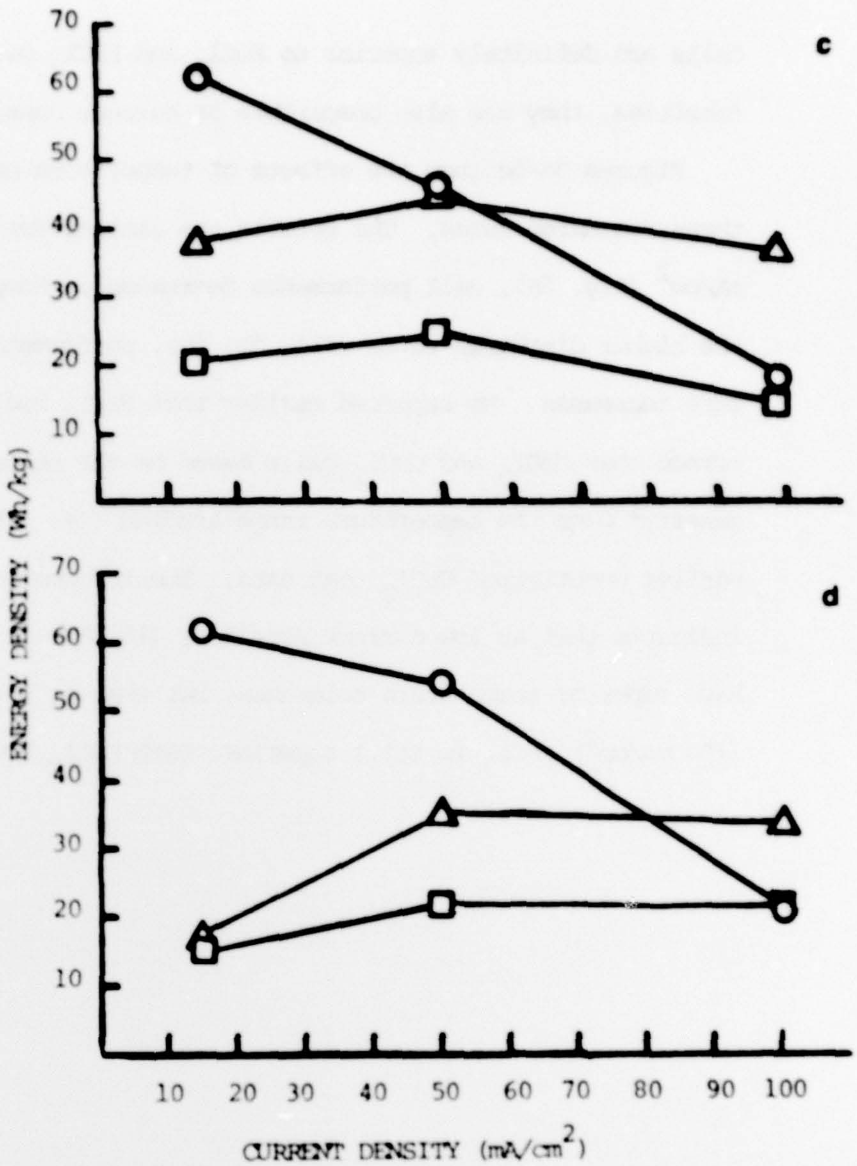

FIGURE 4 (con't)

cells are definitely superior to $MoCl_5$ and $FeCl_3$ cells at very low current densities, they are also comparable at current densities as high as 80 mA/cm^2.

Figures 5a-5c show the effects of temperature on cell performance at three discharge rates. The effects are similar for all cell types. At 15 mA/cm^2 (Fig. 5a), cell performance decreases as temperature increases. At the higher discharge rates (Fig. 5b, 5c), performance increases as temperature increases. We reported earlier that $FeCl_3$ had better temperature tolerance than $MoCl_5$ and $CuCl_2$ cells based on the percent change in energy density* over the temperature range studied (3). This was based on the earlier unoptimized $CuCl_2$ test data. The information shown in Table IV indicates that at low current densities (15 mA/cm^2) optimized $CuCl_2$ cells have superior temperature tolerance, but that at higher current densities (100 mA/cm^2) $FeCl_3$ is still superior, with $CuCl_2$ better than $MoCl_5$.

*The percent change in performance is defined by:

$$\%\ \text{change} = \frac{\text{maximum energy density} - \text{minimum energy density}}{\text{maximum energy density}} \times 100$$

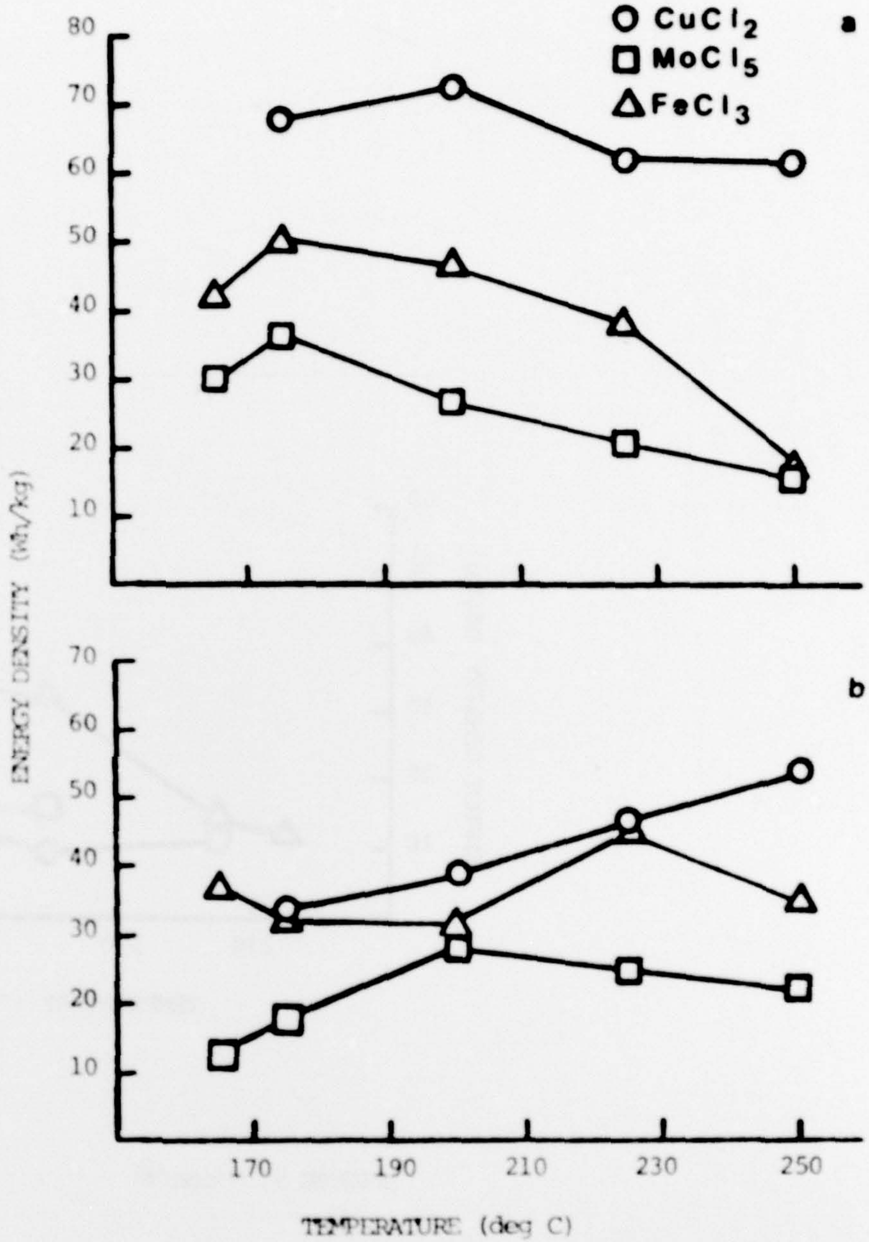

FIGURE 5. Energy Density as a Function of Temperature at a. 15 mA/cm^2, b. 50 mA/cm^2, and c. 100 mA/cm^2.

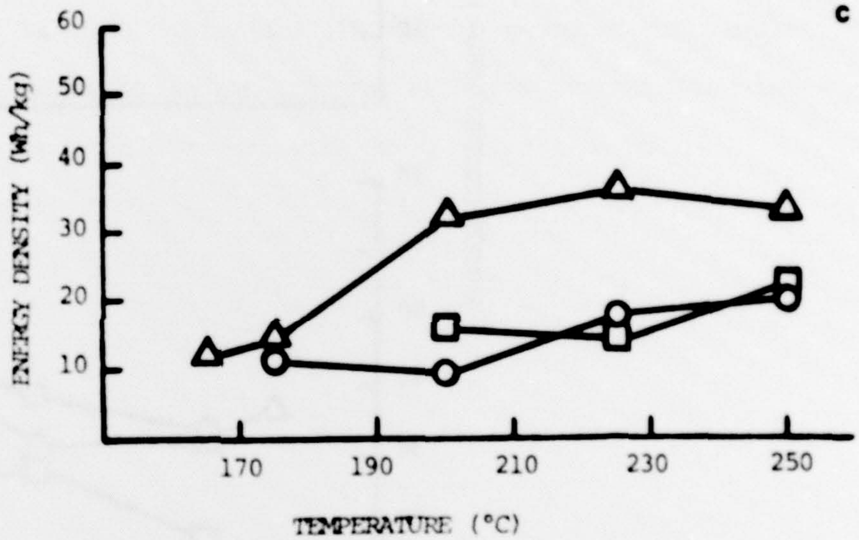

FIGURE 5. (con't)

TABLE IV. Temperature Tolerance of $MoCl_5$, $FeCl_3$, and $CuCl_2$ Thermal Cells

Current Density (mA/cm^2)	Cell	Change in Performance* (%)	Temp. Range (°C)
	$MoCl_5$	58.7	
15	$FeCl_3$	66.0	175-250
	$CuCl_2$	15.7	
	$MoCl_5$	32.5	
100	$FeCl_3$	12.3	200-250
	$CuCl_2$	53.0	

*The percent change in performance is defined as:

$$\% \text{ change} = \frac{\text{Maximum energy density} - \text{minimum energy density}}{\text{maximum energy density}} \times 100$$

A final area investigated with the $CuCl_2$ cells was the effects initial stack pressure has on cell performance. The optimized cells were discharged at initial stack pressures from 6000 kg/m^2 to 21,000 kg/m^2. As seen in Fig. 6, above about 9000 kg/m^2 there is little difference in cell performance. This is similar to $FeCl_3$ cells reported earlier (3) except that for $FeCl_3$ cells the value was 1400 kg/m^2. The difference in the minimum pressures must be due to the different cathode materials since the composition of the cells were otherwise identical.

CONCLUSIONS

An earlier study of the $LiAl/NaAlCl_4/CuCl_2$ system for thermal cells did not consider optimization of cell configuration. Since the appearance of a technical problem with the $LiAl/NaAlCl_4/MoCl_5$ system, $CuCl_2$ has drawn more

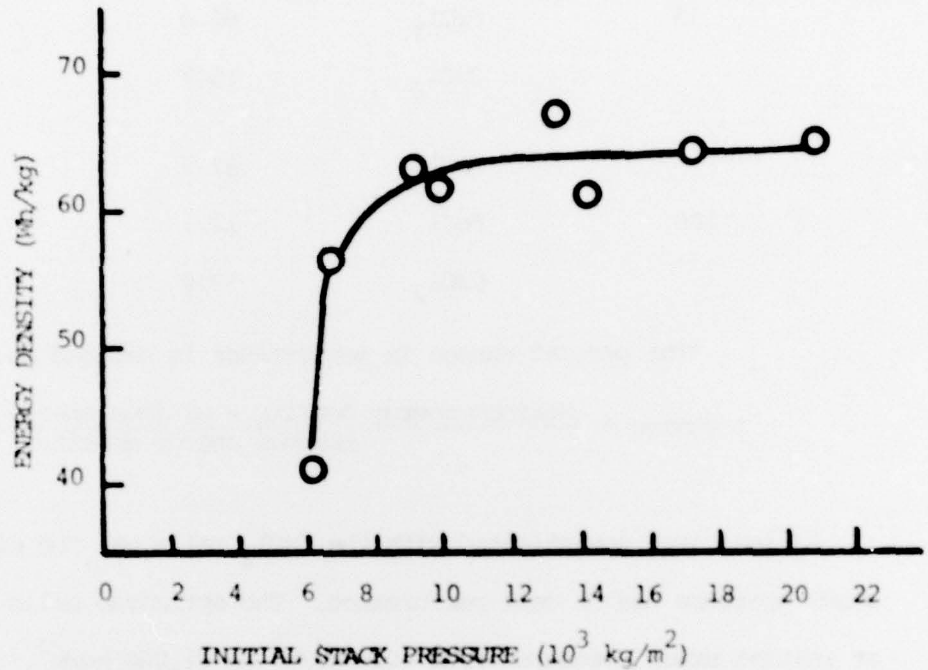

FIGURE 6. Energy Density as a Function of Initial Stack Pressure

attention as a viable cathode material in the $NaAlCl_4$ thermal battery. This study established an optimized configuration for $CuCl_2$ thermal cells, and the discharge characteristics of the optimized cell were determined. This cell delivered 72.6 Wh/kg to 80% ICCV at 200°C and 15 mA/cm^2. This high energy density was obtained as a result of a lifetime of 106 minutes. This energy density is greater than any obtained from $FeCl_3$ and $MoCl_5$ cells. Single cell tests also indicate that $CuCl_2$ cells show good temperature tolerance, especially at low current densities.

Although the optimum operating conditions for $CuCl_2$ cells are low current density and low temperature, they also out perform $FeCl_3$ and $MoCl_5$ cells at current densities as high as 80 mA/cm^2, especially at the higher temperatures. Therefore, $CuCl_2$ cells are not limited to very low current densities as suggested previously.

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